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Atmospheric
Chemistry
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Discussions

Interactive comment on "Why formation rate of 3 nm particles depends linearly on sulphuric acid concentration?" *by* M. Kulmala et al.

Anonymous Referee #2

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General comments:

In this manuscript, a new hypothesis is presented to explain the observed low power-law dependence of the atmospheric nucleation rate on sulphuric acid concentration. The authors name this as "activation theory" and contrast it to two other theories, termed "kinetic" and "thermodynamic" theory. I consider the paper interesting and original enough to be published in Atmospheric Chemistry and Physics. However, there a number of issues that should be handled with more care before the paper will be ready for publication.

Specific comments:

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First of all, I think that the title should be changed. The current title gives the impression that the formation rate of 3 nm particle really depends linearly on H2SO4 concentration. This is clearly not the case, as also admitted by the authors later in the paper. Perhaps the most important message of this paper is that the 3-nm particle formation rate can have a power-law dependency of less than two on the H2SO4 concentration, which is the absolute minimum in case of “kinetic” nucleation or any “thermodynamic” nucleation. The title should reflect this thinking and to be consistent with what is shown in the paper.

The derived relation n1<=n3 on page 11281-82 requires a few clarifications. First, the derivation assumes implicitly some sort of pseudo steady-state situation. What happens if J1 changes very rapidly as could be the case during the morning hours? Apparently, J3 follow changes in J1 with a time lag of about (2 nm/GR), so this can in principle be taken into account. On the other hand, if changes in J1 are driven by a changing H2SO4 concentration, one would expect that also GR changes during this time period (and the time lag between J1 and J3 would not be constant anymore). Would this affect the conclusions? Second, it is assumed that the growth between 1 and 3 nm is driven by condensation only. Would the relation between n1 and n3 be different in a system where coagulation makes a significant contribution to cluster growth? The authors should mention these issues in the paper and address them briefly.

Equation (9) of the activation theory misses a source term for the clusters. I suppose clusters need to come from somewhere, so such a term should be there. The authors should justify why they omitted that term here.

On page 11283 it is stated that Figure 2 indicates a linear dependence H2SO4 concentration and 3-6 nm particle concentration. Clearly, this holds only during a part of the day (about the time period 84.3-84.8). Beyond this time frame, no correlation at all between these two concentrations exists. The authors should mention this and also explain why it is so.

On page 11285 the authors refer to Figure 3 and state that the linear fit (“activation theory”) is much better than the other two fits corresponding to “kinetic” and “thermodynamic” theory. By simply looking at Figure 3, it not clear at all to me that the linear fit is substantially better than the fit with a power-law dependency of two. The linear fit seems to be best during the morning and most of the daytime but it is definitely not the best during the evening. The authors should be more specific here. Preferably, the “goodness” of each fit should be shown by a proper statistical treatment.

Finally, the authors should be more careful about what they eventually claim. Clearly, they provide a plausible explanation for the observed low power-law dependency of atmospheric aerosol formation on sulphuric acid concentration. On the other hand, one single (and not entirely convincing) case is not enough to proof that they really see the hypothesized phenomenon in the atmosphere.

Minor/technical comments:

Page 11285, lines 11-12: Numerical values for the pre-factors Ci are given. How universal are these values?

Page 11285, line 19: “Quite often organic vapours are needed what activation”. This statement may be true but I do not see any justification for saying it like this without some proof.

Figure 1 misses the scales in both X and Y axis. While in principle this phenomenon is independent of the scale, in practise it is not since at very low H2SO4 concentration no particle formation takes place and at very large H2SO4 concentration particle formation is probably so rapid that coagulation starts to take over. This should be brought up somehow.

In Figure 2, it is not explained which curve refers to sulphuric acid and which curve refers to particle concentration.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 11277, 2005.

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